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Optical Study of Second-order Processes Responsible for Formation of Free Polarons in Conjugated Polymers

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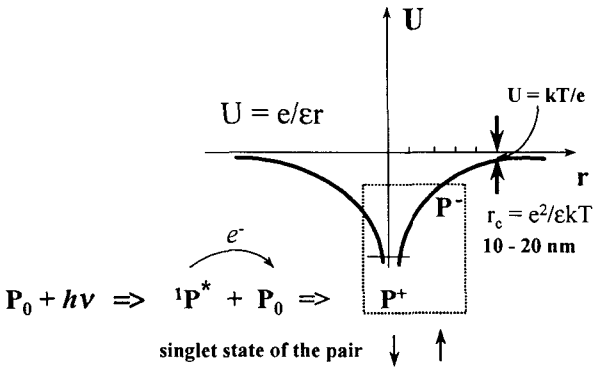
The photoconductivity is known to appear as a result of photogeneration of free charge carriers. However a feature of molecular materials including conjugated polymers with nondegenerated ground state consists in indirect mechanism of their formation. Molecular electron excitation is a primary event, and intermolecular electron transfer occurs afterwards. Charge carriers are formed in pairs, and electron and holes (or negative and positive polarons) find themselves bound together by the Coulomb force, and they require activation energy in order to escape geminate recombination and to become free charge carriers able to take part in the cw electrical conductivity processes. Figure 1 shows schematically the processes involved in the formation of polaron pairs and free charge carriers.



Formation of a polaron pair in an electron-transfer reaction

Figure 1.

Activated process of dissociation of polaron pairs explains the known temperature dependence of the photoconductivity. The latter becomes smaller at lowering the temperature, typical value of activation energy being about 0.2 eV.

Activated dissociation of polaron pair does not appear to be the only way of free carrier formation. Our recent results obtained on substituted polythiophene and polyphenylene vinylene [1] have shown that under the laser pulse excitation a photoconductivity appears, which does not depend on the temperature. It was done by using 150 fs, 400 nm, 1 kHz repetition rate laser pulses. Figure 2 shows a typical dependence of laser pulse induced photoconductivity on the excitation intensity. Amplitude of prompt component is plotted as the ordinate. One can see the dependencies are linear at low intensity of laser pulses, and become quadratic at higher one.

According to the model the charge carriers that are formed primarily belong to polaron pairs, and they can take part in the cw photoconductivity only if geminate recombination is prevented. At low temperature pairs cannot dissociate, and one has to suggest a new mechanism of free carrier formation. We believe that quadratic dependence shown in the Figure 2 is a sequence of inter-pair recombination of charges, which sets free the remaining charges.

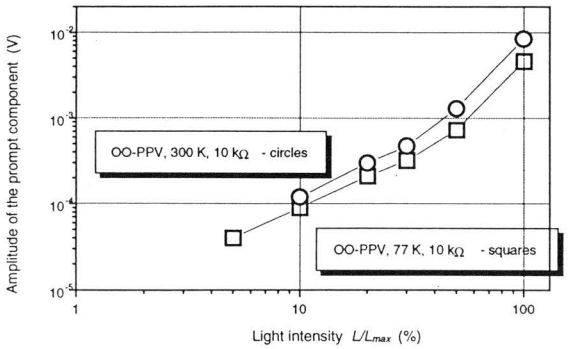


Figure 2. Dependence of the amplitude of the prompt component of the transient signal on the light intensity for OO-PPV, V=500 V. 100% correspond to 130 μJ/pulse [1].

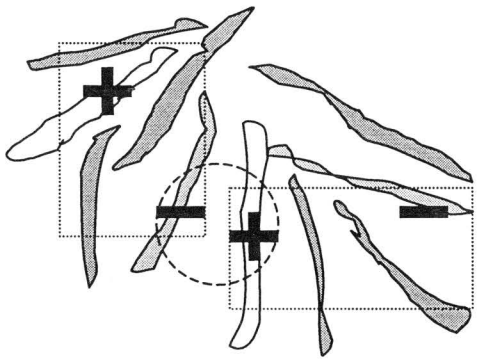


Figure 3 shows the idea. Occasional superposition of two polaron pairs can result in recombination of neighbor charges, which belong to different pairs, thus leaving two remaining charges at higher intercharge distance and helping them to become free. High excitation rate achievable by laser permits to generate a high density of charges. At highest intensity used the light absorption rate in [1] was about 2×10^{19} quantum/cm^{3}pulse.

Figure 3. Schematic view of inter-pair recombination. Two polaron pairs (in dotted frames) are formed in the vicinity of each other. Next neighbor polarons recombine (in dashed circle).

Prompt component of the photoconductivity is believed to originate from a shift of free charge carriers by electric field E before trapping. Reason for that is independence of the mobility μ_l of primarily formed charge carriers on temperature. Estimation of the photoconductivity of that type can be made in the following way. Suppose the total density of charge carriers produced by the laser pulse is n_0, and geminate recombination can be approximated by monomolecular decay with a lifetime τ_{pair}. After the short pulse the next equation permits to calculate the kinetics of the decay of the total density n of charges:

$$\frac{dn}{dt} = -\frac{n}{\tau_{pair}} - k_{rec}n^2 \quad (1)$$

$$n = \frac{n_0 e^{-\frac{t}{\tau_{pair}}}}{1 + n_0 k_{rec}\tau_{pair}(1 - e^{-\frac{t}{\tau_{pair}}})} \quad (2)$$

Charge carriers that recombine randomly can only take part in the cw photoconductivity or in transient photoconductivity measured by the circuit with $RC >> \tau_{pair}$. One can estimate the total amount of charge carriers formed by a single pulse that recombine randomly. If each recombination event sets free α <1 charge carriers, then amount of free carriers, which appeared due to recombination is

$$N_{free} = \alpha \int_0^{\infty} k_{rec} n^2 dt = n_0 \alpha \left[1 - \frac{\ln(1 + n_0 k_{rec} \tau_{pair})}{n_0 k_{rec} \tau_{pair}} \right] \quad (3)$$

They produce a photocurrent pulse that looks after integration by the electrical circuit as a signal

$$u(t) \propto \alpha E \mu_1 \tau_1 N_{free} e^{-\frac{t}{RC}} \quad (4)$$

Here τ_1 is the lifetime of charge carriers before trapping.
Figure 4 shows the dependence of $N_{free}\, k_{rec}\tau_{pair}$ ($\propto$ amplitude of the signal) on the laser pulse energy ($\propto n_0$) calculated by Eq. (3)

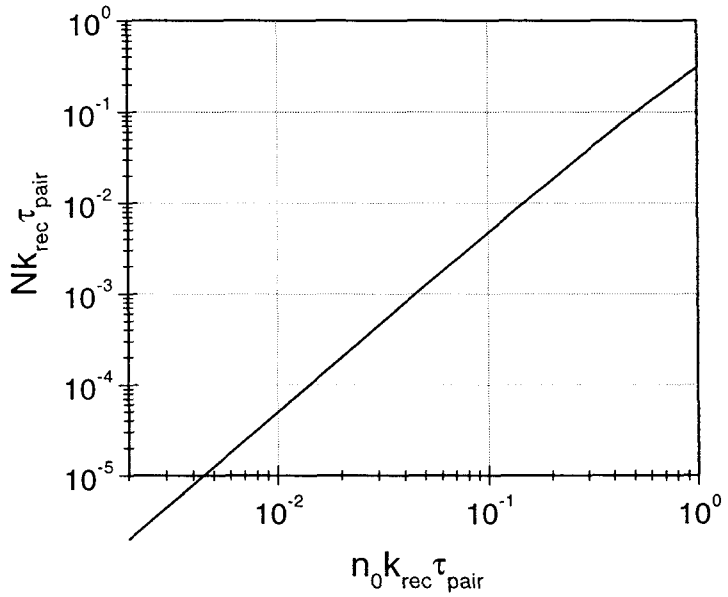


Figure 4. Dependence of the amplitude of the prompt photocurrent component on the number of charge carriers generated by the laser pulse.

Experimental observation of quadratic dependence of the prompt component of the photocurrent on the laser pulse energy will permit approaching to measurement of polaron pair lifetime.
In order to measure lifetimes of species responsible for the formation of free charge carriers we suggest using a two-pulse laser technique. Let us use a pair of δt = 150 fs, $\lambda = 400$ nm laser pulses with the energy that fits for observation of the quadratic dependence. As it follows from our experience it must be about 100 μJ/pulse per cm^2. The pulses must be equal, the second one being delayed in respect to the first one by controlled delay time t within ps to ns time domain. A tentative experimental set-up is shown in Figure 5.

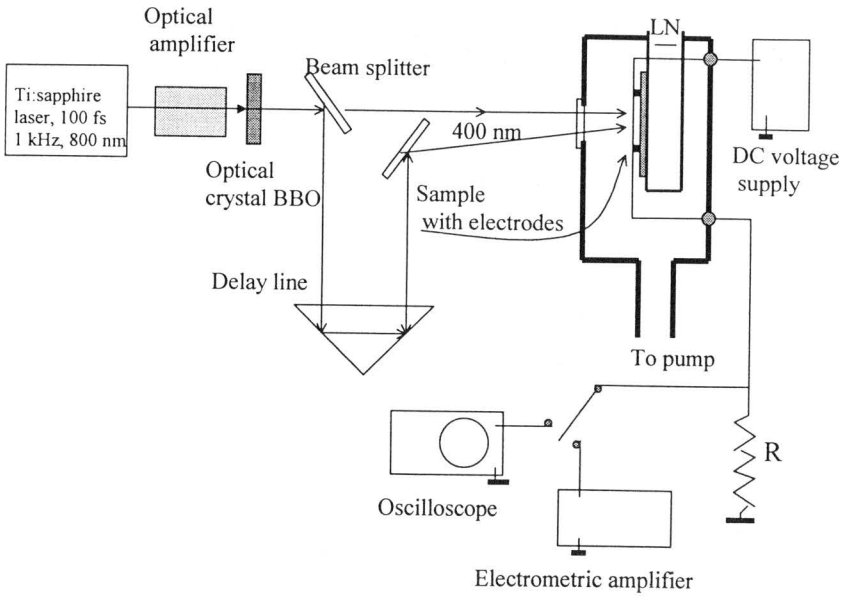


Figure 5. Scheme of experimental set-up.

One can expect as a result of the experiment that the amplitude of the prompt component u will be

$$u \propto 2I^2(1+f(t)) \qquad (5)$$

where $f(t)$ is a function describing the decay of species responsible for the quadratic dependence of prompt component of photoconductivity. For example, it may be an exponent $f(t) = \exp(-\frac{t}{\tau})$. Thus, one has to measure the prompt component of transient photoconductivity as a function of the delay time. There is a real hope that this procedure will allow measuring directly the lifetime of polaron pair. After that one can investigate the dependence of the lifetime on other parameters such as electric field strength, temperature, light intensity, etc.
Experiments in line with that idea are in progress now.

Reference

1. E. Frankevich, H. Ishii, Y. Hamanaka, T. Yokoyama, A.Fujii, S. Li, K. Yoshino, A. Nakamura, K. Seki, *Phys. Rev.* **B** (*in press*).